PATENT SPECIFICATION

NO DRAWINGS

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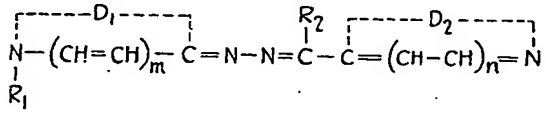
COMPLETE SPECIFICATION

Diazacarbocyanine Bases

We, J. R. GEIGY S.A., a Swiss Company, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new diazacarbocyanine bases.

According to the present invention there are provided new diazacarbocyanine bases of the general formula I:—



. . . I

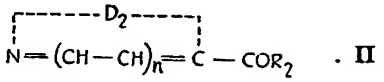
where R_1 is selected from hydrogen, alkyl, aryl and aralkyl groups, R_2 is an alkyl, aryl or aralkyl group, m and n are the same or different and are each nought or one, and D_1 and D_2 are the same or different and are each a residue of a five-membered or six-membered heterocyclic nitrogen nucleus. It is to be understood that the heterocyclic nuclei may be polynuclear, the additional rings being themselves isocyclic. Thus each may contain a fused benzene ring as, for example, in a quinoline nucleus. Phenyl groups and fused isocyclic groups present in the compounds may themselves carry substituent groupings, e.g. alkyl, aryl, alkoxy, hydroxy, amino or acylamino groups or halogen atoms (e.g. chlorine or bromine).

Examples of heterocyclic nuclei of which D_1 and D_2 may be the residue are thiazole, pyridine, pyrimidine, thiadiazole and their partially reduced derivatives (e.g. thiazoline) and the polynuclear derivatives of these, such as benzothiazole, quinoline and benziminazole. Where the residues D_1 and D_2 include tertiary nitrogen atoms of the form $—NR^1—$, R^1 may be hydrogen, alkyl, aryl, or aralkyl.

The group R_1 is preferably hydrogen or an alkyl group containing up to 4 carbon atoms and the group R_2 is preferably an alkyl group containing up to 4 carbon atoms or a phenyl group.

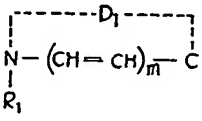
The aforesaid compounds are valuable dyestuffs for polymeric materials consisting essentially of polymers of acrylonitrile and copolymers of acrylonitrile with other monomeric materials. Generally the polymers will contain at least 85 per cent of acrylonitrile units and a particular commercial material of the type, essentially in the form of textile fabric, is sold under the Registered Trade Mark ORLON. Such polymers are difficult to dye by the use of conventional dyestuffs and the compounds of the present invention provide a new class of dyestuff of exceptional value in the dyeing of such materials. The dyeing may be effected from solution in a dilute acid medium or from dispersion.

According to a further feature of the invention compounds of general formula I are prepared by condensing together a ketone of the general formula II:—



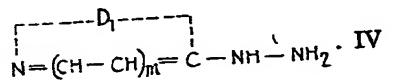
. II

with a hydrazine derivative of the formula III:—



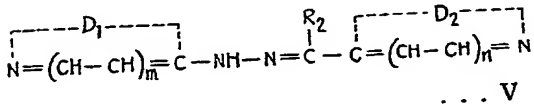
. III

It is to be observed that where, in the compound of formula III, R_1 is a hydrogen atom, the compounds may be regarded as simple heterocyclic hydrazines of formula IV:—



. IV

and the compounds of formula I which are provided therefrom can therefore be written in the tautomeric form of formula V:—



. . . V

The condensation is preferably effected in the presence of a diluent, e.g. ethanol, and it is advantageous to have present an acid catalyst, e.g. acetic acid. The condensation is accelerated by heating the reagents together and the diazacarbocyanine base can then usually be isolated by cooling the reaction mixture. Alternatively, it can be caused to separate by adding a diluent in which the product is insoluble, e.g. water or diethyl ether.

According to a further feature of the invention a compound of general formula I wherein R_1 is an alkyl group may be prepared from a compound of general formula V by alkylation, for example, with an alkyl halide (e.g. iodide) in the presence of a base, e.g. an alcoholic solution of caustic alkali.

Suitable intermediates of formula II are as follows (throughout the Specification temperatures given are in degrees Centigrade):—

2-Benzoyl-1-methylbenziminazole

Mandelic acid (12.4 g.), *o*-methylaminoaniline (6.8 g.), water (35 ml.) and concentrated hydrochloric acid (22 ml.) were boiled under reflux for 40 minutes. After cooling, the solution was made alkaline with ammonia to precipitate an oil which solidified on scratching and was recrystallised from aqueous ethanol to give 1-methyl-2-α-hydroxybenzylbenziminazole as buff needles, m.pt. 157°.

The above alcohol (5.0 g.) was dissolved in acetic acid (34 ml.) and a solution of sodium dichromate (2.7 g.) in water (8 ml.) added. The mixture was boiled under reflux for 35 minutes, diluted with water (50 ml.) and made alkaline with ammonia to precipitate an oil which rapidly solidified. Recrystallisation from ethanol gave 2-benzoyl-1-methylbenziminazole as white needles, m.pt. 66—7°.

2-Acetyl-1-methylbenziminazole.

By the above process 2 - α - hydroxyethyl - 1 - methylbenziminazole (buff needles, m.pt. 86—7° from water) was prepared from *o*-methylaminoaniline and lactic acid, and oxidised to give 2 - acetyl - 1 - methylbenziminazole (white microcrystals, m.pt. 64—5° from water).

2-Acetylquinoline

Pulverised sodium (4.1 g.) and dry toluene (50 ml.) were stirred and ethanol (8.3 ml.) added and the mixture boiled under reflux for 1 hour. A mixture of ethyl quinaldinate (24.1 g.) and dry ethyl acetate (15.8 g.) was added in two portions. A solid separated rapidly and after 1 minute the mixture became too thick to stir. After heating in an oil bath at 115° for 6½ hours, the solid was filtered off, ground with ether and dried in air. The solid (39.5 g.) was then added to a mixture of concentrated sulphuric acid (30 ml.) and water (915 ml.) and the mixture heated on a steam bath for 7 hours. The mixture was then made alkaline with sodium hydroxide and steam distilled to give 2 litres of distillate. On cooling the distillate gave 2-acetylquinoline as a colourless solid, m.pt. 51°.

2-Benzoylbenzothiazole

o-Aminothiophenol (62.5 g.) and mandelic acid (76 g.) were heated in a 1 litre wide-necked flask in an oil bath at 140—150° for 3 hours. The mixture was cooled and the resulting thick gum dissolved in benzene. On shaking the benzene solution with N-sodium hydroxide (2 × 100 ml.), a solid was precipitated which was filtered off and recrystallised from benzene to give 2α-hydroxybenzylbenzothiazole as colourless needles, m.pt. 121°.

The alcohol (28 g.) thus obtained was dissolved in acetic acid (258 ml.) and a solution of sodium dichromate (16.3 g.) in water (43 ml.) added. The mixture was boiled under reflux for 45 minutes and added to water (1.5 litres) to precipitate a solid which was filtered off and recrystallised from ethanol to give 2-benzoylbenzothiazole as white needles, m.pt. 102°.

2-Benzoylbenziminazole

Mandelic acid (50 g.), *o*-phenylene diamine (24 g.), water (140 ml.) and concentrated hydrochloric acid (88 ml.) were boiled under reflux for 40 minutes. The mixture was diluted with water, cooled and excess ammonia added to give a white precipitate which was filtered off and recrystallised from aqueous ethanol to give 2-α-hydroxybenzylbenziminazole as white needles, m.pt. 207—8°.

The product was oxidised as above to yield 2-benzoylbenziminazole as colourless needles from ethanol, m.pt. 214—5°.

2-Acetylbenzothiazole

In a similar manner to that used for 2-benzoylbenzothiazole, lactic acid and *o*-aminothiophenol gave 2-α-hydroxyethylbenzothiazole, b.pt. 140—160° at 1 mm. which then crystallised and was recrystallised from cyclohexane to give pale yellow needles, m.pt. 62—3°, and oxidation of this alcohol gave 2-acetylbenzothiazole from ethanol as colourless needles, m.pt. 111—112°.

2-Acetylbenziminazole

In a similar manner to that used for 2-benzoylbenziminazole, lactic acid and *o*-phenylene diamine gave 2-α-hydroxyethylbenziminazole from water as colourless needles, m.pt. 181—2° and 2-acetylbenziminazole from water as colourless leaflets, m.pt. 180—1°.

2-Benzoylpyridine was prepared by the method of Wolffenstein and Hartwich, Berichte, 1915, *48*, 2047.

4-Benzoylpyridine was obtained from isonicotinyl chloride by a method similar to that used to prepare the 2-compound. It was obtained as a colourless solid, b.pt. 179—184° at 15 mm., m.pt. 70°.

2-Propionylbenzothiazole

o-Aminothiophenol (19.2 g.) and α-hydroxy-n-butyric acid (17.5 g.) were heated in an oil bath at 140° for 4 hours and the temperature in the reaction mixture then raised during 1 hour to 200°. The mixture was then distilled under vacuum collecting, after a forerun, from 150—80° at 1 mm. The distillate slowly solidified and was recrystallised from cyclohexane to give 2-α-hydroxypropylbenzothiazole as colourless leaflets, m.pt. 90—92°. This alcohol (5.0 g.) was dissolved in acetic acid (46.5 ml.) and a solution of sodium dichromate (3.7 g.) in water (9.4 ml.) added. The mixture was boiled under reflux for 1 hour and diluted with water (150 ml.). An oil was precipitated which slowly acidified on cooling and was filtered off and recrystallised from cyclohexane to give the pure compound as pale yellow needles, m.pt. 97°.

2-Phenylacetylquinoline

Sodium (3.0 g.) was pulverized and placed under dry toluene (35 ml.). While stirring and heating in an oil bath at 120°, ethanol (8.0 ml.) was added and when the sodium was no longer visible a mixture of ethyl quinaldinate (20 g.) and ethyl phenylacetate (18.9 g.) were added. The mixture was heated and stirred for a further 6 hours and then cooled. After dilution with ether (100 ml.), the precipitated solid was filtered off, washed well with ether and dried. The solid was added to a mixture of water (50 ml.) and concentrated hydrochloric acid (12.4 ml.) and the mixture boiled under reflux for 1 hr. and cooled to precipitate a sticky solid. This solid was filtered off and mixed with 2N sodium carbonate (200 ml.) when some of the material dissolved and the remainder became nicely crystalline. Addition of excess potassium carbonate to the hydrochloric acid solution gave a little more solid and the combined non-acidic solids were filtered off and recrystallised from ethanol to give the pure ketone as colourless needles, m.pt. 110—2°.

Suitable intermediates of formula III are obtainable by methods known in the literature. The following, referred to later herein, do not appear to have been previously described.

2-Hydrazono-1,2-dihydro-methyl quinoline

1-Methylquinoline-2-thione (17.2 g.) and methyl toluene-p-sulphonate (18.3 g.) were heated at 100° for ½ hour. Water (50 ml.), ethyl hydrazinoformate (10.2 g.) and triethylamine (10.9 g.) were added and the mixture boiled under reflux for ½ hour. The mixture was filtered hot to remove a red solid and the filtrate cooled to precipitate an orange crystalline mass which was filtered and dried, 15.3 g., m.pt. 110—113°. The compound (9.5 g.) and concentrated hydrochloric acid (50 mol.) were boiled under reflux for 8 hours. The resulting colourless solution was diluted with water and basified with excess ammonia to give a red solid which, after cooling, was filtered off and dried, giving the pure hydrazone, m.pt. 125—7°.

6-Ethoxy-2-hydrazono-3-methylbenzthiazoline

6-Ethoxy-2-methylthiobenzothiazole (21 g.) and methyl toluene-p-sulphonate (17.8 g.) were fused at 140—160° for 1½ hours. The resulting solid was dissolved in ethanol (100 ml.) and ethyl hydrazinoformate (10 g.) and triethylamine (14 ml.) added. The mixture was boiled under reflux for 1½ hours to give a white solid which, after cooling, was filtered off and washed well with water. After drying the carbethoxyhydrazone compound was obtained as white needles, m.pt. 169—71° (resolidifying and finally melting at 279—81°), 24.5 g.

This material may be hydrolysed either:

(a) The substance (10 g.) and concentrated hydrochloric acid (50 ml.) were boiled under reflux for 5 hours. After dilution with water (100 ml.), excess ammonia was added to precipitate a solid which was filtered off and recrystallised from ethanol to give pure hydrazone as off-white needles, m.pt. 142°.

(b) The substance (10 g.), ethanol (10 ml.), 40% sodium hydroxide (10 ml.) and water (20 ml.) were boiled under reflux for 4 hours. After dilution with water (50 ml.), the precipitated solid was filtered off and recrystallised from ethanol to give the pure product, m.pt. 142°.

The following carboethoxyhydrazones and

hydrazones were prepared by methods analogous to the above process; hydrolysis was achieved by methods (a) and (b) as indicated.

2 - Hydrazono-6-methoxy-3-methylbenzothiazoline was obtained (b), via the carboethoxy hydrazone (m.pt. 303°), from ethanol as colourless needles, m.pt. 156—8°.

2 - Hydrazino - 5:6 - dimethoxy-3-methylbenzothiazoline was obtained (b), via the carboethoxyhydrazone (m.pt. 249°), as colourless needles, m.pt. 163—5°.

2 Hydrazono - 3 - methyl - 5 - methylthio - Δ^4 - 1:3:4 - thiadiazoline was obtained (b), via the carboethoxyhydrazone (m.pt. 104°), from ethanol as colourless needles, m.pt. 83—84°.

2 - Hydrazono - 5 - chloro - 3 - methylbenzothiazoline was obtained (b), via the carboethoxyhydrazone (m.pt. 231°), as pale yellow needles from benzene, m.pt. 138—40°.

4 - hydrazono - 1:4 - dihydro - 1 - methylquinoline

4-Methylthioquinoline (5.1 g.) and methyl toluene-*p*-sulphonate (6.0 g.) were fused at 150° for 1 hour. The resulting melt was dissolved in water (50 ml.) and hydrazine hydrate (100%) (5.0 ml.) added. The mixture was heated at 100° for 1 hour and cooled to precipitate an oil which rapidly solidified and was recrystallised from benzene-ethanol to give the pure hydrazone as buff needles, m.pt. 100°.

2 - Hydrazino - 4.6 - dimethyl - pyrimidine was prepared by treating hydrazine hydrate with 2 - chloro-4.6-dimethyl - pyrimindine in ethanol. Recrystallisation from water yields a product in form of needles which melt at 165° C.

3-Hydrazino-6-phenyl-pyridazine was obtained by treating hydrazine hydrate with 3-chloro-6-phenyl-pyridazine in ethyl alcohol. Recrystallisation from methanol yields needles with m.pt 144° C.

The following Examples will serve to illustrate the invention:—

EXAMPLE 1

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 1 - methyl - 2 - benziminazolylbenzylidene) hydrazine.

2 - Benzoyl - 1 - methyl - benziminazole (2.21 g.) and 3 - methyl - 2 - hydrazonobenzothiazoline (1.79 g.) (Fuchs and Grauaug, ber., 1928, *61*, 57) were dissolved in hot ethanol (12 ml.) and acetic acid (1.0 ml.) added to the solution. After boiling for 5 minutes, the solution was cooled to precipitate a solid which was recrystallised from ethanol to give the *product* as pale yellow plates, m.pt. 142—5°.

EXAMPLE 2

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 1 - methyl - 2 - benziminazolylethylidene) hydrazine

2 - Acetyl - 1 - methylbenziminazole (1.74 g.) and 3 - methyl - 2 - hydrazonobenzothiazoline (1.79 g.) were dissolved in hot ethanol (12 ml.) and acetic acid (1.0 ml.) added. After boiling for five minutes a solid was precipitated and, after cooling, was filtered off and recrystallised from ethanol to give the *product* as pale yellow needles, m.pt. 188—9°.

EXAMPLE 3

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - pyridylethylidene) hydrazine

2 - Acetylpyridine (2.47 g.) (Pinner, Ber., 1901, *34*, 4240) and 3-methyl-2-hydrazonobenzothiazoline (3.6 g.) were dissolved in hot ethanol (20 ml.) and acetic acid (2.0 ml.) added. After boiling for ten minutes the solution was cooled to give a crystalline solid which was filtered off and recrystallised from benzene-light petroleum to give the *product* as very pale yellow rhombs, m.pt. 135°.

EXAMPLE 4

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 4 - pyridylethylidene) hydrazine

4-Acetylpyridine (2.02 g.) (Pinner, *ibid.* 4250) and 3 - methyl - 2 - hydrazonobenzothiazoline (3.0 g.) were dissolved in hot ethanol (30 ml.) and acetic acid (2.0 ml.) added. The solution was boiled for 5 minutes, cooled and diluted with water to precipitate a solid which was filtered off and recrystallised from benzene to give the *product* as pale yellow needles, m.pt. 188°.

EXAMPLE 5

1 - (3 - Ethyl - 2 - benzothiazolinylidene)-2-(α - 2 - quinolylethylidene) hydrazine

2-Acetylquinoline (1.71 g.) and 3-ethyl-2-hydrazonobenzothiazoline (1.94 g.) (Fuchs and Grauaug *loc. cit.*) were dissolved in hot ethanol (20 ml.) and acetic acid (1.0 ml.) added to the solution. After refluxing for 4 minutes the solution was cooled to precipitate a solid which was filtered off and recrystallised from 50—50 benzene ethanol to give the *product* as yellow leaflets, m.pt. 127°

EXAMPLE 6

1 - (3 - Ethyl - 2 - benzothiazolinylidene) - 2-(α - 2 - benzothiazolylbenzylidene) hydrazine

2-Benzoylbenzothiazole (2.39 g.) and 3-ethyl-2-hydrazonobenzothiazoline (1.94 g.) were dissolved in hot ethanol (20 ml.) and acetic acid (1.0 ml.) added to the mixture. After boiling under reflux for 3 minutes the solution was cooled to precipitate an oil which on scratching became solid. This solid was filtered off and recrystallised from 50—50 ethanol benzene to give the *product* as yellow needles, m.pt. 175—177°.

EXAMPLE 7

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - benzothiazolylbenzylidene) hydrazine

2-Benzoylbenzothiazole (2.39 g.) and 3-methyl-2-hydrazonobenzothiazoline (1.79 g.)

were dissolved in hot ethanol (20 ml.) and acetic acid (1.0 ml.) added. After boiling under reflux for 3 minutes the solution was cooled to precipitate a solid which was filtered off and recrystallised from ethyl acetate to give the *product* as yellow needles, m.pt. 193°.

EXAMPLE 8

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2-(α - 2 - benziminazolylbenzylidene) hydrazine

2 - Benzoylbenziminazole (2.5 g.). and 3-methyl - 2 - hydrazonobenzothiazoline (2.8 g.) were dissolved in hot ethanol (60 ml. and acetic acid (5.1 ml.) added. After boiling under reflux for 5 minutes the mixture was diluted with water to give a yellow solid which was recrystallised from benzene to give the *product* as yellow needles, m.pt. 236—237°.

EXAMPLE 9

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2-(α - 2 - benzothiazolylethylidene hydrazine

2-Acetylbenzothiazole (6.9 g.) and 3-methyl - 2 - hydrazonobenzothiazoline (7.0 g.) were dissolved in hot ethanol (100 ml.) and acetic acid (10 ml.) added. After refluxing for 3 minutes, the mixture was cooled to give a yellow solid which was filtered off and recrystallised from benzene to give the *product* as yellow needles, m.pt. 215°.

EXAMPLE 10

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - benziminazolylethylidene hydrazine

2 - Acetylbenziminazole (2.5 g.) and 3-methyl - 2 - hydrazonobenzothiazoline (2.8 g.) were dissolved in hot ethanol (60 ml.) and acetic acid (5.1 ml.) added. After boiling under reflux for 5 minutes, the mixture was cooled to give a solid which was filtered off and recrystallised from ethanol to give the *product* as pale yellow needles, m.pt. 236—7°.

EXAMPLE 11

1 - (2 - Benzothiazolyl) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine

2-Hydrazinobenzothiazole (1.65 g.) (Boggust and Cocker), J. Chem. Soc., 1949, 362) and 2-acetylbenzothiazole (1.77 g.) were dissolved in ethanol (20 ml.) and acetic acid (1.0 ml.) added. After boiling for 20 minutes the solution was cooled to give a solid which was filtered off and recrystallised from 85% ethanol to give the *product* as pale yellow leaflets, m.pt. 203—5°.

EXAMPLE 12

1 - (2 - Benziminazolyl) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine

In a similar manner to that of Example 11, 2-hydrazinobenziminazole (United States Patent No. 2,073,600) and 2-acetylbenzothiazole gave the *product* from ethanol as yellow leaflets, m.pt. 280—2°.

EXAMPLE 13

1 - (3 - Ethyl - 2 - benzothiazolinylidene) - 2-(α - 2 - benzothiazolylethylidene) hydrazine.

2 - Acetylbenzothiazole (0.69 g.) and 3-ethyl - 2 - hydrazonobenzothiazoline (0.7 g.) were heated with ethanol (10 ml.) and acetic acid (1.7 ml.) for 4 minutes on a steam bath. On cooling, a solid was precipitated which was filtered off and recrystallised from ethanol to give the *product* as yellow needles, m.pt. 151—2°.

The following diazacarbocyanine bases were prepared from the appropriate intermediates by methods similar to that of Example 3.

EXAMPLE 14

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 4 - pyridylbenzylidene) hydrazine was obtained from ethanol as yellow microneedles, m.pt. 153—6°.

EXAMPLE 15

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - quinolyl - β - phenylethylidene) hydrazine was obtained from benzene as pale yellow microcrystals, m.pt. 199—201°.

EXAMPLE 16

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - benzothiazolylpropylidene) hydrazine was obtained from cyclohexane as pale yellow needles, m.pt. 88—90°.

EXAMPLE 17

1 - (6 - Ethoxy - 3 - methyl - 2 - benzothiazolinylidene) - 2 - (α - 4 - pyridylethylidene) hydrazine was obtained from ethanol as greenish-yellow plates, m.pt. 124°.

EXAMPLE 18

1 - (1:2 - Dihydro - 1 - methyl - 2-quinolinylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was obtained from benzene as orange plates, m.pt. 158°.

EXAMPLE 19

1 - (6 - Methoxy - 3 - methyl - 2 - benzothiazolylinylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was obtained from ethanol as yellow microneedles, m.pt. 190°.

EXAMPLE 20

1 - (5:6 - Dimethoxy - 3 - methyl - 2-benzothiazolinylidene) - (2 - (α - 2 - benzothiazolylethylidene) hydrazine was obtained from ethanol as small yellow plates, m.pt. 193°.

EXAMPLE 21

1 - (3 - Methyl - 5 - methylthio - 2 - Δ^4-1:3:4 - thiadiazolinylidene) - 2 - (α - 2-benzothiazolylethylidene) hydrazine was obtained from ethanol as small yellow needles, m.pt. 176°.

EXAMPLE 22

1 - (1:2 - Dihydro - 1 - methyl - 2-quinolinylidene) - 2 - (α - 4 - pyridylbenzylidene) hydrazine was obtained from ethanol as orange microcrystals, m.pt. 143°.

EXAMPLE 23

1 - (6 - Ethoxy - 3 - methyl - 2 - benzo-

thiazolinylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was obtained from ethanol as greenish yellow needles, m.pt. 181°.

EXAMPLE 24

1 - (4:6 - Dimethyl - 2 - pyrimidyl) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was obtained from ethanol as pale yellow needles, m.pt. 155—6°.

EXAMPLE 25

1 - (6 - Phenyl - 3 - pyridazinyl) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was purified by boiling out with ethanol to give the *product* as small yellow needles, m.pt. 259°.

EXAMPLE 26

1 - (5 - Chloro - 3 - methyl - 2 - benzothiazolinylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was purified by boiling out with ethanol and obtained as pale yellow needles, m.pt. 197—9°.

EXAMPLE 27

1 - (1:4 - Dihydro - 1 - methyl - 4 - quinolinylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was obtained from ethanol as small yellow needles, m.pt. 248—9°.

EXAMPLE 28

1 - (3 - Methyl - 2 - benzothiazolinylidene) - 2 - (α - 2 - quinolylbenzylidene) hydrazine

3 - Methyl - 2 - hydrazonobenzothiazoline (2.15 g.) and 2-benzoylquinoline (Besthorn, Berichte, 1908, *41*, 2002) (2.8 g.) were dissolved in hot ethanol (30 ml.) and acetic acid (1.5 ml.) added. The mixture was boiled under reflux for 15 minutes and cooled to precipitate a gum which slowly solidified. Recrystallisation of this solid from ethanol gave the *product* as yellow needles, m.pt. 163—5°.

EXAMPLE 29

1 - (3 - Methyl - 2 - benzothiazolinylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine.

1 - (2 - Benzothiazolyl) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine (0.65 g.) (prepared as described in Example 11), methanol (15 ml.) and 10% aqueous sodium hydroxide (1.0 ml.) were boiled under reflux to give a deep orange solution. Methyl iodide (1.0 ml.) was added and the mixture boiled for 20 minutes to give a pale yellow solution. The mixture was cooled to precipitate a solid which was filtered off and washed well with methanol containing alkali until the washings were no longer orange. Recrystallisation of the remaining solid from benzene gave the pure *product* as yellow needles, m.pt. 215°, identical with that of Example 9.

EXAMPLE 30

1 - (1:2 - Dihydro - 1 - methyl - 4:6 - dimethyl - 2 - pyrimidylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was similarly obtained by methylating the product of Example 24 and was recrystallised from light petroleum (b.p. 60—80°) as yellow needles, m.pt. 119—122°.

EXAMPLE 31

1 - (2:3 - Dihydro - 2 - methyl - 6 - phenyl - 3 - pyridazinylidene) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine was similarly obtained from the product of Example 25 and recrystallised from cyclohexane as small orange needles, m.pt. 190—2°.

EXAMPLE 32

This example illustrates the dyeing of polyacrylonitrile fibres with the dyestuffs of the present invention:—

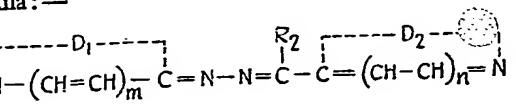
0.5 Parts of the dyestuff obtained according to Example 1 are pasted with 0.5 parts of acetic acid (80%) and dissolved by the addition of 4000 parts of hot water. One further part of 80% acetic acid and 4 parts of a condensation product from olein alcohol and 15 mols of ethylene oxide are added and 100 parts of polyacrylonitrile fibres are entered. The bath is heated within 30 minutes to 90°, kept for 10 minutes at this temperature and then dyeing is performed at the boil for 1 hour. The dyebath is almost completely exhausted. The dyed goods are then soaped for 15 minutes at 80° in 5000 parts of water with the addition of a sulphonated fatty acid condensation product, rinsed and dried. The polyacrylonitrile fibres are dyed in pure yellow shades which have excellent fastness to washing and light.

The preferred compounds of the present invention are those of Example 8 and 10.

The present invention accordingly includes the new compounds of formula I and tautomeric formula V, their production by the methods described, the dyeing of textile materials, particularly polyacrylonitrile materials, by means of said compounds and the dyed materials so obtained.

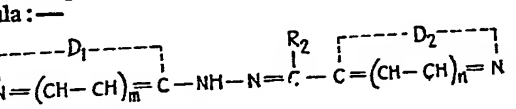
WHAT WE CLAIM IS:—

1. Diazacarbocyanine bases of the general formula:—



where R_1 is selected from hydrogen, alkyl, aryl and aralkyl groups, R_2 is an alkyl, aryl or aralkyl group, m and n are the same or different and are each nought or one, and D_1 and D_2 are the same or different and are each a residue of a five-membered or six-membered heterocyclic nitrogen nucleus.

2. Diazacarbocyanine bases according to claim 1 wherein R_1 is a hydrogen atom and the compounds have the tautomeric formula:—



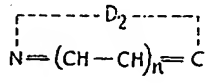
3. Diazacarbocyanine bases according to claim 1 wherein R_1 is an alkyl group containing up to 4 carbon atoms.

4. Diazocarbocyanine bases according to claim 1 or 2 wherein R_2 is an alkyl group containing up to 4 carbon atoms or a phenyl group.

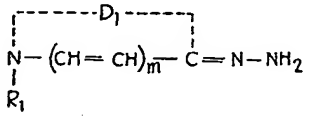
5. 1 - (3 - Methyl - 2 - benzothiazolinylidene) - 2 - (α - 2 - benziminazolylbenzylidene) hydrazine.

6. 1 - (3 - Methyl - 2 - benzothiazolinylidene) - 2 - (α - 2 - benziminazolylethylidene) hydrazine.

7. A process for the production of a diazacarbocyanine base as defined in claim 1 which comprises condensing together a ketone of the formula:—



and a hydrazine derivative of the formula:—



8. A process according to claim 7 wherein the condensation is effected in the presence of a diluent and an acid catalyst.

9. A process for the production of a diazacarbocyanine base as defined in claim 1 wherein R_1 is an alkyl group, which comprises subjecting to alkylation a compound of the formula set forth in claim 2.

10. A process according to claim 9 wherein the alkylation is effected by treatment with an alkyl halide in the presence of a base.

11. A process for dyeing polymeric materials comprising at least 85% of acrylonitrile units which comprises subjecting said materials to treatment with a solution in a dilute acid medium, or with a dispersion of a diazacarbocyanine base as defined in any of claims 1—6.

12. Polymeric materials comprising at least 85% of acrylonitrile units dyed with a diazacarbocyanine base as defined in any of claims 1—6.

13. A diazacarbocyanine base according to claim 1 or 2 as specifically set forth in any one of the foregoing specific Examples 1—7, 9 and 11—31.

14. A process for the production of a diazacarbocyanine base as defined in claim 1 or 2 substantially as set forth in any one of the foregoing specific Examples 1 to 31.

15. A process according to claim 11 substantially as set forth in the foregoing specific Example 32.

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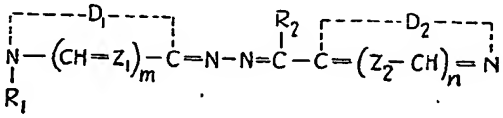
PROVISIONAL SPECIFICATION

Diazacarbocyanine Bases

We, J. R. GEIGY S.A., a Swiss Company, of Basle, Switzerland, do hereby declare this invention to be described in the following statement:—

This invention relates to new diazacarbocyanine bases.

According to the present invention there are provided new diazacarbocyanine bases of the general formula I:—



. . . I

wherein R_1 is selected from hydrogen, alkyl, aryl, aralkyl, hydroxyalkyl and carboxyalkyl groups, R_2 is an alkyl, aryl or aralkyl group, Z_1 and Z_2 are the same or different and are each a methine (—CH=) group or a nitrogen atom, m and n are the same or different and are each nought or one, and D_1 and D_2 are the same or different and are each a residue of a five-membered or six membered heterocyclic nitrogen nucleus. It is to be understood that the heterocyclic nuclei may be polynuclear, the additional rings being themselves heterocyclic or isocyclic. Thus each may contain a fused benzene ring as, for example, in a quinoline nucleus. Phenyl groups and fused isocyclic or heterocyclic groups present in the compounds may themselves carry substituent groupings, e.g., alkyl, aryl, alkoxy, hydroxy, amino or acylamino groups or halogen atoms (e.g. chlorine or bromine).

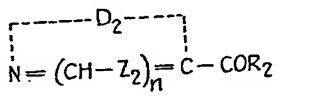
Examples of heterocyclic nuclei of which D_1 and D_2 may be the residue are oxazole, thiazole, selenazole, pyridine, pyrrolenine, glyoxaline, pyrimidine, pyrazole, thiadiazole, triazole and their partially reduced derivatives (e.g. thiazoline) and the polynuclear derivatives of these, such as benzothiazole, quinoline, indolenine, benziminazole and quinazoline. Where the residues D_1 and D_2 include tertiary nitrogen atoms of the form —NR^1—, R^1 may be hydrogen, alkyl, aryl or aralkyl.

The Group R_1 is preferably hydrogen or an alkyl or hydroxyalkyl group containing

up to 4 carbon atoms and the group R_2 is preferably an alkyl group containing up to 4 carbon atoms or a phenyl group.

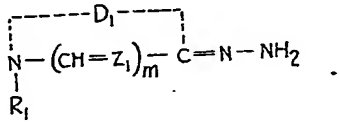
The aforesaid compounds are valuable dyestuffs for polymeric materials consisting essentially of polymers of acrylonitrile and copolymers of acrylonitrile with other monomeric materials. Generally the polymers will contain at least 85 per cent of acrylonitrile units and a particular commercial material of the type, essentially in the form of textile fabric, is sold under the trade name ORLON. Such polymers ar difficult to dye by the use of conventional dyestuffs and the compounds of the present invention provide a new class of dyestuff of exceptional value in the dyeing of such materials. The dyeing may be effected from solution in a dilute acid medium or from dispersion.

According to a further feature of the invention compounds of general formula I are prepared by condensing together a ketone of the general formula II:—



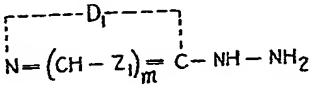
. . II

with a hydrazine derivative of the formula III:—



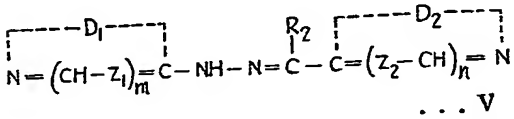
. . III

It is to be observed that where, in the compound of formula III, R_1 is a hydrogen atom, the compounds may be regarded as simple heterocyclic hydrazines of formula IV:—



. . IV

and the compounds of formula I which are provided therefrom can therefore be written in the tautomeric form of formula V:—



. . . V

The condensation is preferably effected in the presence of a diluent, e.g. ethanol, and it is advantageous to have present an acid catalyst, e.g. acetic acid. The condensation is accelerated by heating the reagents together and the diazacarbocyanine base can then usually be isolated by cooling the reaction mixture. Alternatively, it can be caused to separate by adding a diluent in which the product is insoluble, e.g. water or diethyl ether.

The following Examples will serve to illustrate the invention:—

EXAMPLE 1

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 1 - methyl - 2 - benziminazolylbenzylidene) hydrazine.

a) Mandelic acid (12.4 g.), *o*-methylaminoaniline (6.8 g.), water (35 ml.) and concentrated hydrochloric acid (22 ml.) were boiled under reflux for 40 minutes. After cooling, the solution was made alkaline with ammonia to precipitate an oil, which solidified on scratching and was recrystallised from aqueous ethanol to give 1-methyl-2-α-hydroxybenzylbenziminazole as buff needles, m.pt. 157°.

b) The above alcohol (5.0 g.) was dissolved in acetic acid (34 ml.) and a solution of sodium dichromate (2.7 g.) in water (8 ml.) added. The mixture was boiled under reflux for 35 minutes, diluted with water (50 ml.) and made alkaline with ammonia to precipitate an oil which rapidly solidified. Recrystallisation from ethanol gave 2-benzoyl-1-methylbenziminazole as white needles, m.pt. 66—7°.

c) 2 - Benzoyl - 1 - methylbenziminazole (2.21 g.) and 3 - methyl - 2 - hydrazonobenzothiazoline (1.79 g.) (Fuchs and Grauaug, Ber., 1928, *61*, 57) were dissolved in hot ethanol (12 ml.) and acetic acid (1.0 ml.) added to the solution. After boiling for 5 minutes, the solution was cooled to precipitate a solid which was recrystallised from the *product* as pale yellow plates, m.pt. 142—5°.

EXAMPLE 2

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 1 - methyl - 2 - benziminazolylethylidene) hydrazine.

a) By the process of a) and b) of Example 1, 2 - α - hydroxyethyl - 1 - methylbenziminazole (buff needles, m.pt. 86—7° from water) was prepared from *o*-methylaminoaniline and lactic acid, and oxidised to give 2 - acetyl - 1 - methylbenziminazole (white microcrystals, m.pt. 64—5° from water).

b) 2 - Acetyl - 1 - methylbenziminazole (1.74 g.) and 3 - methyl - 2 -hydrazonobenzothiazoline (1.79 g.) were dissolved in hot ethanol (12 ml.) and acetic acid (1.0 ml.) added. After boiling for five minutes a solid was precipitated and, after cooling, was filtered off and recrystallised from ethanol to give the *product* as pale yellow needles, m.pt. 188—9°.

EXAMPLE 3

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - pyridylethylidene) hydrazine.

2-Acetylpyridine (2.47 g.) (Pinner, Ber., 1901, *34*, 4240) and 3-methyl-2-hydrazono-

benzothiazoline (3.6 g.) were dissolved in hot ethanol (20 ml.) and acetic acid (2.0 ml.) added. After boiling for ten minutes the solution was cooled to give a crystalline solid which was filtered off and recrystallised from benzene-light petroleum to give the *product* as very pale yellow rhombs, m.pt. 135°.

EXAMPLE 4

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 4 - pyridylethylidene) hydrazine.

4-Acetylpyridine (2.02 g.) (Pinner, *ibid.* 4250) and 3-methyl - 2 - hydrazonobenzothiazoline (3.0 g.) were dissolved in hot ethanol (30 ml.) and acetic acid (2.0 ml.) added. The solution was boiled for 5 minutes, cooled and diluted with water to precipitate a solid which was filtered off and recrystallised from benzene to give the *product* as yellow needles, m.pt. 188°.

EXAMPLE 5

1 - (3 - Ethyl - 2 - benzothiazolinylidene)-2 - (α - 2 - quinolylethylidene) hydrazine.

a) Pulverised sodium (4.1 g.) and dry toluene (50 ml.) were stirred and ethanol (8.3 ml.) added and the mixture boiled under reflux for 1 hour. A mixture of ethyl quinaldinate (24.1 g.) and dry ethyl acetate (15.8 g.) was added in two portions. A solid separated rapidly and after 1 minute the mixture became too thick to stir. After heating in an oil bath at 115° for 6 hours, the solid was filtered off, ground with ether and dried in air. The solid (39.5 g.) was then added to a mixture of concentrated sulphuric acid (30 ml.) and water (915 ml.) and the mixture heated on a steam bath for 7 hours. The mixture was then made alkaline with sodium hydroxide and steam distilled to give 2 litres of distillate. On cooling the distillate gave 2-acetylquinoline as a colourless solid, m.pt. 51°.

b) 2-Acetylquinoline (1.71 g.) and 3-ethyl - 2 - hydrazonobenzothiazoline (1.94 g.) (Fuchs and Grauaug *loc cit.*) were dissolved in hot ethanol (20 ml.) and acetic acid (1.0 ml.) added to the solution. After refluxing for 4 minutes the solution was cooled to precipitate a solid which was filtered off and recrystallised from 50—50 benzene ethanol to give the *product* as yellow leaflets, m.pt. 127°.

EXAMPLE 6

1 - (3 - Ethyl - 2 - benzothiazolinylidene)-2 - (α - 2 - benzothiazolylbenzylidene) hydrazine.

a) *o*-Aminothiophenol (62.5 g.) and mandelic acid (76 g.) were heated in a 1 litre wide-necked flask in an oil bath at 140—150° for 3 hours. The mixture was cooled and the resulting thick gum dissolved in benzene. On shaking the benzene solution with N-sodium hydroxide (2 × 100 ml.), a solid was precipitated which was filtered off and recrystallised from benzene to give 2-α-hydroxybenzylbenzothiazole as colourless needles, m.pt. 121°.

b) The alcohol (28 g.) was dissolved in acetic acid (258 ml.) and a solution of sodium dichromate (16.3 g.) in water (43 ml.) added. The mixture was boiled under reflux for 45 minutes and added to water (1.5 litres) to precipitate a solid which was filtered off and recrystallised from ethanol to give 2-benzoylbenzothiazole as white needles, m.pt. 102°.

c) 2-Benzoylbenzothiazole (2.39 g.) and 3 - ethyl - 2 - hydrazonobenzothiazoline (1.94 g.) were dissolved in hot ethanol (20 ml.) and acetic acid (1.0 ml.) added to the mixture. After boiling under reflux for 3 minutes the solution was cooled to precipitate an oil which on scratching became solid. This solid was filtered off and recrystallised from 50—50 ethanol benzene to give the *product* as yellow needles, m.pt. 175—177°.

EXAMPLE 7

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - benzothiazolylbenzylidene) hydrazine.

2-Benzoylbenzothiazole (2.39 g.) (prepared as Example 6, stages a) and b)) and 3-methyl-2-hydrazonobenzothiazoline (1.79 g.) were dissolved in hot ethanol (20 ml.) and acetic acid (1.0 ml.) added. After boiling under reflux for 3 minutes the solution was cooled to precipitate a solid which was filtered off and recrystallised from ethyl acetate to give the *product* as yellow needles, m.pt. 193°.

EXAMPLE 8

1 - (3 - Methyl - 2 - benzothiazolinylidene)-(2 - (α - 2 - benziminazolylbenzylidene) hydrazine.

a) Mandelic acid (50 g.), *o*-phenylene diamine (24 g.), water (140 ml.) and concentrated hydrochloric acid (88 ml.) were boiled under reflux for 40 minutes. The mixture was diluted with water, cooled and excess ammonia added to give a white precipitate which was filtered off and recrystallised from aqueous ethanol to give 2 - α - hydroxybenzylbenziminazole as white needles, m.pt. 207—8°.

b) The alcohol oxidised in a similar fashion to that of stage b) of Example 6, to give 2-benzoylbenziminazole from ethanol as colourless needles, m.pt. 214—5°.

c) 2-Benzoylbenziminazole (2.5 g.) and 3-methyl - 2 - hydrazonobenzothiazoline (2.8 g.) were dissolved in hot ethanol (60 ml.) and acetic acid (5.1 ml.) added. After boiling under reflux for 5 minutes the mixture was diluted with water to give a yellow solid which was recrystallised from benzene to give the *product* as yellow needles, m.pt. 236—237°.

EXAMPLE 9

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - benzothiazolylethylidene) hydrazine.

a) In a similar manner to that of Example 6, stages a) and b), lactic acid and *o*-amino-

thiophenol gave 2 - α - hydroxyethylbenzothiazole, b.pt. 140—165° at 1 mm. which then crystallised and was recrystallised from cyclohexane to give pale yellow needles, m.pt. 62—3°, and oxidation of this alcohol gave 2-acetylbenzothiazole from ethanol as colourless needles, m.pt. 111—112°.

b) 2-Acetylbenzothiazole (6.9 g.) and 3-methyl-2-hydrazonobenzothiazoline (7.0 g.) were dissolved in hot ethanol (100 ml.) and acetic acid (10 ml.) added. After refluxing for 3 minutes, the mixture was cooled to give a yellow solid which was filtered off and recrystallised from benzene to give the *product* as yellow needles, m.pt. 215°.

EXAMPLE 10

1 - (3 - Methyl - 2 - benzothiazolinylidene)-2 - (α - 2 - benziminazolylethylidene) hydrazine.

a) In a similar manner to that of Example 8, stages a) and b), lactic acid and *o*-phenylene diamine gave 2 - α - hydroxyethylbenziminazole from water as colourless needles, m.pt. 181—2° and 2 - acetylbenziminazole from water as colourless leaflets, m.pt. 180—1°.

b) 2-Acetylbenziminazole (2.5 g.) and 3 - methyl - 2 - hydrazonobenzothiazoline (2.8 g.) were dissolved in hot ethanol (60 ml.) and acetic acid (5.1 ml.) added. After boiling under reflux for 5 minutes, the mixture was cooled to give a solid which was filtered off and recrystallised from ethanol to give the product as pale yellow needles, m.pt. 236—7°.

EXAMPLE 11

1 - (2 - Benzothiazolyl) - 2 - (α - 2 - benzothiazolylethylidene) hydrazine.

2-Hydrazinobenzothiazole (1.65 g.) (Boggust and Cocker, J. Chem. Soc., 1949, 362) and 2-acetylbenzothiazole (1.77 g.) (made as in Example 9, stage a)) were dissolved in ethanol (20 ml.) and acetic acid (1.0 ml.) added. After boiling for 20 minutes the solution was cooled to give a solid which was filtered off and recrystallised from 85% ethanol to give the *product* as pale yellow leaflets, m.pt. 203—5°.

EXAMPLE 12

1 - (2 - Benziminazolyl) - 2 - (α - benzothiazolylethylidene) hydrazine.

In a similar manner to that of Example 11, 2 - hydrazinobenzoiminazole (U.S.P. 2,073,600) and 2-acetylbenzothiazole (see Example 9, stage a)) gave the *product* from ethanol as yellow leaflets, m.pt. 280—2°.

EXAMPLE 13

1 - (3 - Ethyl - 2 - benzothiazolinylidene)-2 - (α - 2 - benzothiazolylethylene) hydrazine.

2-Acetylbenzothiazole (0.69 g.) (obtained as in Example 9, stage a)) and 3 - ethyl - 2-hydrazonobenzothiazoline (0.7 g.) were heated with ethanol (10 ml.) and acetic acid (1.7 ml.) for 4 minutes on a steam bath. On cooling, a solid was precipitated which was filtered off and recrystallised from ethanol to give the product as yellow needles, m.pt. 151—2°.

The present invention accordingly includes the new compounds of formula I and tautomeric formula V, their production by the method described, the dyeing of textile materials, particularly poly - acrylonitrile materials, by means of said compounds and the dyed materials so obtained.

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